

Composite Material and Use of a Composite Material

The present invention relates to a composite material with a specific filler and the  
5 use of a composite material with a specific filler for dental purposes.

Background of the invention

Composite materials are composites made from a plastics material and inorganic  
10 filling materials. Conventionally, therefore, they consist primarily of three different  
components: a polymerisable organic matrix, filler particles and an agent which  
ensures the bond between the polymer and the filler particles. Dental restorative  
materials represent a specific form of composite materials as they are subjected to  
the greatest demands, due to the extreme physical and chemical stress in the  
15 extremely inhospitable environment of the mouth. Due to their extensive  
requirement profile, these materials often serve as a basis for developing non-dental  
composites or as a model for use in the non-dental field.

Dental restorative composite materials have been used for over 40 years for fillings,  
20 linings and fixings, as stump restoration, crown and bridge, prosthesis and relining  
material, as filled adhesives which produce adhesion on dental enamel, plastics,  
ceramics or metal, and as dental sealing compositions. After being introduced into  
the cavity, composites cure in a polymerisation reaction, either chemically or by the  
addition of external energy.

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The organic polymerisable component of the dental composite material is generally  
cross-linked in a radical reaction and contains corresponding ethylenically  
unsaturated functional groups. The monomers and oligomers comprise mono-, di-  
and/or polyacrylates and/or methacrylates, such as for example  
30 diglycidylmethacrylate of bisphenol A ('Bis-GMA', 2,2-bis[4(2-hydroxy-3-  
methacryloxypropyloxy)-phenyl]propane) and diurethane di(meth)acrylate from

2,2,4-Trimethylhexamethylenediisocyanate and 2-hydroxyethyl(meth)acrylate (UDMA). When referring to methacrylates, analogous acrylates are also understood. Commercially obtainable standard mixtures contain Bis-GMA, UDMA and triethyleneglycoldimethacrylate to reduce the viscosity.

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In order to be able to carry out radical curing of the resin composition, an initiator system is added to the mass which triggers the radical polymerisation following radiation and/or a redox reaction process. A typical system which initiates the radical polymerisation of the methacrylate consists of a photoinitiator (ketone) and  
10 an accelerator (amine). Typically, camphorquinone is used as a ketone and para N,N-Dimethylaminobenzoic acid as an amine. Further photoactive components can be admixed to the mixture. If the composition is exposed to light with a suitable radiation source at 460nm, the composite material is photochemically cross-linked. Alternatively, the material can also be chemically cross-linked. To this end, the  
15 peroxide/tertiary amine combination is used as a redox system. The two components have to be kept separated from one another in a 2-component system. After mixing the two components free radicals are generated and the radical polymerisation of the acrylates cures the composite material. As no external aids are required with this type of curing, this system is also known as self-curing.

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Composite compositions can therefore be designed as either self-curing or photochemically curing (mono-cure). Furthermore, composite compositions can be formulated which represent a combination of self-curing and photochemically curing systems (dual-cure). If polyacrylic acid or a derivative of polyacrylic acid is  
25 added to one part of the 'dual-cure' composite system and basic glass is present in the other part, under suitable conditions, this system also cures in an acid base reaction (triple-cure) in addition to a chemical and photochemical mechanism.

The inorganic filling materials of the dental composite material generally consist of quartz, borosilicate glass, lithium aluminium silicate, barium aluminium silicate, strontium/barium glass, zinc glass, zirconium silicate, pyrogenic or colloidal silicic acid.

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The bond of the inorganic filling materials with the organic resin matrix is generally ensured by the use of coupling agents or adhesion promoters. This is essential for the subsequent suitability of the composite mass as a dental material. In this connection, the filler, generally in the presence of weak acids, is treated with a silane before it is mixed with the liquid resin component. The method for preparing silanized filler surfaces consists in firstly adjusting an ethanol/water mixture (generally 95/5% by volume) with acetic acid to a pH value of 4.5 - 5.5. The silane is then added in such an amount that a solution strength of ca. 2% results. Within 5 minutes the alkoxysilyl groups are hydrolysed and the siloxane formation commences. Then the filler to be processed is added to the solution by continuous mixing. Within a few minutes the silane is adsorbed by the filler and the surface of the filling material loaded with adhesion promotor. The solution is decanted off and the particles washed twice with ethanol. Finally, the remaining silanol functions are condensed for a few minutes at 110 DEG C and 24 hours at room temperature.

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The silane acts as a surface active material which compatibilises the surface of the filler with the resin matrix and ensures a rigid bond between the organic and inorganic material. Amongst others, 3-methacryloyloxypropyltrimethoxysilane has proved to be a particularly suitable silane for creating a bond between the inorganic and organic phase. A portion of the hydrolysed alkoxysilyl groups of the silane reacts directly with the hydroxyl groups on the mineral surface of the filler, while the other portion fuses together and thus produces a continuous layer of the coupling agent on the filler surface. During the course of the subsequent radical polymerisation of the dental composite mass, the methacryloyloxypropyl functions

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of the silane layer continuously adhering to the filler surface are then polymerised in the organic resin phase and thus form a permanent bond between the hydrophilic fillers and the hydrophobic resin matrix.

- 5 The properties of the resulting dental composite material is determined primarily by the inorganic phase. Whilst Young's modulus (E-module) for an unfilled resin system based on Bis-GMA is 2.8 GPa, the dental enamel has a value of 83 GPa and the dentine a value of 19 GPa. By adding a conventional silylated filler to the Bis-GMA-resin the value of 2.8 GPa can be markedly improved. If the filler is added to  
10 the resin in the volume ratio of 1 to 1.25, Young's modulus can be raised to a value of 10 GPa. For a ratio of 1:1 a value of 15 GPa can be achieved.

- The type of filler, the amount and distribution of particles for a given resin composition determine the mechanical, aesthetic and rheological characteristics of  
15 the dental composite moulded material, such as surface hardness, abrasion resistance, wear resistance, pressure resistance, tensile strength, polymerisation shrinkage, fracture resistance and thermal shock resistance as well as polishability, shine, opacity, translucence and colour stability as well as flow characteristics, stability and modelability. As a rule of thumb, the higher the concentration of  
20 silanized filler in the liquid resin, the better the mechanical, physical and chemical properties of the cured moulded material.

- Against the background of the paramount importance of the inorganic phase for the properties of dental composite materials, the traditional division of dental composite  
25 materials is understood to be into three different basic groups.

A macrofilled composite material is a highly filled composition (up to 87 wt.%) with relatively large particles (1-100 $\mu$ m). Whilst previously, glass powder with average particle sizes of 30-50 $\mu$ m served as the filler, nowadays the filler is generally ground

quartz or even glass ceramics with an average particle size of 8-12 $\mu$ m. Macrofilled composites have the best wear resistance, but due to the particle size high polishing is extremely difficult. During polishing the bulky filler particles break out of the filling, small holes remain behind and the broken-out filler fragments exert an  
5 abrasive effect on the remaining moulded material, so that macrofilled composites cannot be highly polished and have a fundamental aesthetic flaw.

In order to comply with the demand for improved aesthetics, the group of microfilled dental composite materials was developed. A characteristic feature of  
10 these groups is the exceptionally small particle size of the composite filler which primarily consists of amorphous silicic acid and has an average particle size of ca. 0.04 $\mu$ m. This small particle size results in an extremely large particle surface which, due to intensive interaction forces between the particle surfaces, in turn sets a premature limit for the filler concentration of the composite material. As a rule,  
15 microfilled composite materials cannot be mixed with filler of more than 50 wt.%, as the material is then no longer workable due to higher viscosity. This composite group may be highly polished, exhibits excellent refractive properties and fulfils all criteria of an exceptionally aesthetically effective dental material. As a result of the low filler content, microfilled materials, compared to macrofilled dental composites,  
20 however, exhibit considerably reduced mechanical properties such as abrasion, tensile strength, excessive shrinkage, etc.

It has been attempted on many occasions, but until now without success, to increase the filler content, for example by the incorporation of pyrogenic silicic acid into  
25 prepolymerised resin particles (25 $\mu$ m), agglomerated or sintered particles and thus to increase the strength.

By attempting to combine the polishability of the microfilled composites with the excellent mechanical properties of the macrofilled composites, the group of so-called hybrid composites was developed. In this connection, the filler used is a mixture of conventional glass with a particle size of 0.6-1.5 $\mu$ m and of nanoscale particles of 0.01-0.05 $\mu$ m. As a rule, the quantifiable portion of nanoscale silicic acid particles is 7-15 wt.%. The entire filler content can be up to 80 wt.%. Due to large variations in the particle sizes, an exceptionally compact packing density of the filler particles can be achieved, smaller particles being located in the spaces between the larger particles.

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An example for the composition of a microfilled system is disclosed in DE 2403211. Hybrid materials are known from the patents DE 2405578, DE 3403040 and EP 382033.

15 US 4,839,215 discloses hollow cylindrical filler particles and dental composite materials with these fillers, the fillers being mechanically linked via the binder and thus the mechanical properties of the polymerisable composite materials improve. The known filler particles have a circular cylindrical form. The central aperture of the particles is between 500 and 1000 $\mu$ m and preferably between 150 to 400 $\mu$ m, most preferably between 225 and 300 $\mu$ m. The external diameter of the particles is under 3 $\mu$ m, preferably between 425 and 200 $\mu$ m, more preferably between 500 and 1000 $\mu$ m and most preferably around 925 $\mu$ m. The ceramic particles are preferably produced by pressing. Further production methods are extrusion, casting, isostatic pressing, hot pressing, injection moulding and depositing onto a mould. The rough  
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25 filler particles only allow composite materials to be produced which have low strength, low hardness, low abrasion resistance and poor polishability.

#### Object of the Invention

Although, due to improvements in materials science, modern composite fillers are a permanent fixture in the treatments available to dentists, even in the side tooth area, these systems nevertheless have several fundamental drawbacks which are primarily  
5 linked with the 'bond' between the organic resin matrix and the inorganic filler surfaces. The silane coupling agents form 'siloxane bonds' with minerals. These bonds which ensure the bond between the two phases, may be hydrolysed, like any bond between an organic polymer and a hydrophilic, mineral material surface. Hydrolysis of the siloxane bond however produces hydrolytic degradation in the  
10 polymer, increased crack formation along the material/resin interfacial region, water absorption, softening effects in the polymer, swelling of the composite, reduced wear resistance, abrasion resistance and colour stability, due to the filler breaking out. Finally, the bond of the two phases is broken.

15 The advantage of silane relative to other adhesion promoters lies in its characteristic of behaving in a reversible manner with regard to hydrolytic bond cleavage. The thermodynamic equilibrium lies broadly on the side of the siloxane bond formation. Although the equilibrium amount of water molecules is therefore more important on the polymer/solid interface layer than the diffusion rate of the water in the polymer,  
20 water entering the material will however set the hydrolytic degradation process in motion. In the presence of strongly hydrophobic resins, water itself reaches the polymer/solid interface by diffusion. Once the interface layer is attacked, the water is attached there in the form of clusters, the bond of the organic phase to the inorganic phase is loosened and the structure of the composite broken up by osmotic  
25 pressure.

To improve the bond between filler and polymer matrix, the possibility was considered to create a physical adhesion in addition to the chemical adhesion. In US 4215033 a semi-porous filler is produced by etching glass. Microporous fillers for

use as dental materials are known from the publications US 4217264, EP 4868, EP 172513, DE 19846556 and DE 19615763. With the physical adhesion, resin penetrates into the pores of the filler and thus after polymerisation anchors the organic with the inorganic phase, as the cured resin is held tightly in the pores of the  
5 filler. Thus an improved structural integrity of the moulded material is ensured.

The principle of the physical anchoring of filler and matrix which is disclosed in DE 19615763 and includes the use of porous SiO<sub>2</sub> particles, has however three principal disadvantages. The first consists of the extremely expensive production of the  
10 porous filling materials which includes a very expensive phase separation step, and grinding and screening processes. The second disadvantage lies in the very small pore diameter which is preferably 90-100 nanometers. In order to ensure an effective inflow of the resin into the pores, resin composites of very low viscosity must be used with low surface tension. This is obtained by the use of dimethacrylates with a  
15 low molecular weight, such as for example triethyleneglycoldimethacrylate (TEDMA) or hexanedioldimethacrylate (HDDMA). A higher proportion of these low molecular monomers leads however to increased composite shrinkage. Alternatively, the viscosity of the matrix can also be reduced by the addition of monomethacrylates, such as for example hydroxypropylmethacrylate (HPMA) or  
20 triethyleneglycolmonoethylethermonomethacrylate. The use of monomethacrylates leads to a poorer cross-linking of the polymer, compared to dimethacrylates and thus to lower flexural strength and greater discolouration. The third disadvantage lies in the restriction of the production process to silicon dioxide fillers which do not allow a clinically acceptable radiopacity to be set.

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In spite of enormous improvements in the field of dental composite materials, the problem of the phase bond however remains unsolved, as even with the use of porous fillers, it can lead to the release of the polymer matrix from the inorganic filler by means of hydrolytic cleavage. It is therefore the object of the invention to



provide a filler which forms a stable bond with the organic phase and allows such a strong physical bond between it and the binder of the dental material that possible hydrolysis can no longer destroy the bond once it is formed, and a composite material containing this filler which, due to the stable bond between the phases, ensures improved properties relative to the prior art.

#### Detailed description of the Invention

The object is achieved by a composite material according to claim 1 and by a composite material according to claim 2. Advantageous embodiments of the invention are disclosed in the sub-claims.

The invention relates to a specific filler with filler particles which comprise a spherical annular structure and structurally correspond to the geometry of a torus. In contrast to porous fillers, in which the resin is merely mechanically anchored in the pores of the filler particles, here the extreme case is realised where the filler is completely drawn through by a single pore. This leads to the organic phase being continually bonded with the inorganic phase and thus forms a particularly effective linkage from a mechanical point of view. In this connection, the torus-shaped filler particles are mechanically penetrated by binders, like a string of beads, and bonded to one another by the continuous resin phase present in the interior of the torus, such that they can no longer be released from the resin matrix by hydrolytic degradation. Thus a dental material is produced which, due to the extremely effective bond between the organic and inorganic composite phase, has a particularly pronounced abrasion resistance with high flexural strength at the same time, which cannot be achieved by comparable dental materials of the prior art. As the hydrolytic degradation which starts over a period of time, also no longer leads to a phase separation because of the solid phase bond, the durability of the dental material is extended with full functionality. At the same time the aesthetic character of the

dental mass is also increased. During polishing the filler particles, due to the solid phase bond with the binder, are worn away in layers and not, as with macrofilled composites, broken as a whole from the polymer matrix. This allows a high polish.

Claims

1. Composite material with a polymerisable organic binder and a filler in a quantity of 1 to 90 wt.%, characterised in that it contains filler particles  
5 obtained by spray drying, which have the shape of a torus and an average external diameter in the region of 0.5-100µm.
2. Composite material with a polymerisable organic binder, characterised in that it contains a filler with filler particles, which have the shape of a torus  
10 and an average external diameter in the region of 0.50-100µm and in that it additionally contains a silica sol.
3. Composite material according to claim 2, characterised in that the filler particles with the shape of a torus are obtained by spray drying.  
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4. Composite material according to either claim 2 or 3, characterised in that the filler contains 50 to 100 wt.% of the filler particles with the shape of a torus.
5. Composite material according to any of claims 1 to 4, characterised in that  
20 the filler contains additional fragment-shaped and/or spherical inorganic filler particles.
6. Composite material according to any of claims 1 to 5, characterised in that the filler additionally contains non-torus-shaped filler particles made from  
25 silicon dioxide.
7. Composite material according to claim 6, characterised in that the non-torus-shaped filler particles are produced from pyrogenic and/or precipitated silicic

acid and/or silicon dioxide sols and/or from a dispersion of pyrogenic and/or precipitated silicic acid.

- 5      8.      Composite material according to any of claims 1 to 7, characterised in that the torus-shaped and/or non-torus-shaped filler particles are silanized.
- 10     9.      Composite material according to any of claims 1 to 8, characterised in that the organic binder includes at least one of the following materials: ethylenically unsaturated monomers and oligomers, epoxides, ormocers, ceramers, liquid crystal systems, spiro-orthoesters, oxethane, polyurethane, polyester, A-silicon and C-silicon, polycarbonic acids.
- 15     10.     Composite material according to any of claims 1 to 9, characterised in that the organic binder cures chemically and/or photochemically.
- 20     11.     Composite material according to any of claims 1 to 10, characterised in that the torus-shaped filler particles have an average external diameter in the region of 1 and 50 $\mu$ m.
- 25     12.     Composite material according to any of claims 1 to 11, characterised in that the torus-shaped filler particles have an internal diameter in the region of 0.2-20 $\mu$ m.
13.     Composite material according to claim 12, characterised in that the torus-shaped filler particles have an internal diameter in the region of 0.4-4.0 $\mu$ m.
14.     Composite material according to any of claims 1 to 13, characterised in that it contains 15-70 wt.% filler with torus-shaped filler particles.

15. Composite material according to any of claims 1 to 14, characterised in that the filler particles contain silicon dioxide and/or heavy metal oxides with an atomic number of greater than 28.
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16. Composite material according to claim 15, characterised in that the heavy metal oxides are selected from the group of zirconium oxide, cerium oxide, tin oxide, zinc oxide, yttrium oxide, strontium oxide, barium oxide, lanthanum oxide, bismuth oxide and compounds thereof.
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17. Dental composite material according to any of claims 1 to 16.
18. Use of a filled and polymerisable composite material which contains a filler with filler particles which have the shape of a torus, in particular according to any of claims 1 to 17, as a dental material.
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